Review

Received: 29 September 2009 Revised: 11 January 2010 Accepted: 18 January 2010 Published online in Wiley Interscience: 3 March 2010

(www.interscience.wiley.com) DOI 10.1002/jsfa.3916

Role of mineral nutrition in minimizing cadmium accumulation by plants

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Abstract

Cadmium (Cd) is a highly toxic heavy metal for both plants and animals. The presence of Cd in agricultural soils is of great concern regarding its entry into the food chain. Cadmium enters into the soil–plant environment mainly through anthropogenic activities. Compounds of Cd are more soluble than other heavy metals, so it is more available and readily taken up by plants and accumulates in different edible plant parts through which it enters the food chain. A number of approaches are being used to minimize the entry of Cd into the food chain. Proper plant nutrition is one of the good strategies to alleviate the damaging effects of Cd on plants and to avoid its entry into the food chain. Plant nutrients play a very important role in developing plant tolerance to Cd toxicity and thus, low Cd accumulation in different plant parts. In this report, the role of some macronutrients (nitrogen, phosphorus, sulfur and calcium), micronutrients (zinc, iron and manganese), and silicon (a beneficial nutrient) has been discussed in detail as to how these nutrients play their role in decreasing Cd uptake and accumulation in crop plants.

Keywords: accumulation; cadmium; edible parts; macronutrients; micronutrients; silicon

INTRODUCTION

Among all the heavy metals, cadmium (Cd) is considered to have high toxicity to humans and all other living organisms as it has no known biological functions in aquatic or terrestrial organisms.[1] Recent advances in industry and agriculture have led to an increased level of Cd in the agricultural soil environment. Cadmium enters the soil through various anthropogenic sources including application of phosphate fertilizers, waste water, Cd-contaminated sewage sludge and manures, and anthropogenic emissions from power stations, metal industries, urban traffic and cement industries.[2–5] Due to its high mobility in soils, Cd accumulation in plants grown on Cd-contaminated soils poses a serious threat to human and animal health.[6] High concentrations of Cd in rice and drinking water play havoc in *Itai-Itai* patients by lowering glomerular rates.[7,8]

Cadmium enters the human body from many sources, i.e. soil, water, air, plants and animals,[9] but the main source of Cd in non-occupational people except smokers is the consumption of Cd-contaminated food.[10] Although it affects a number of organs in the human body, Cd mainly accumulates in the human kidney with a biological half-life of about 10–30 years (depending on the age), and causes renal tubular damage and pulmonary emphysema.[11] Calcium (Ca) metabolism in humans and other vertebrates is also disturbed by Cd, and thus causes hypercalciuria and the formation of kidney stone.[12,13] Kinetics studies carried out in the recent past have clarified that dietary Cd is absorbed by duodenum enterocytes, and only part of the ^{109}Cd is moved to the liver and kidneys by the end of the 64-day 'chase' period.[14,15] The Cd metal, once taken up by the human body, is excreted slowly at a rate of about 0.005% of the body weight.[11]

Ingestion of crops containing high amounts of Cd may contribute substantial Cd to the human diet.[16] Of primary concern is its transfer from vegetables to the body, because vegetables contribute ≥70% of Cd intake in humans.[11] The joint FAO/WHO Expert Committee on Food Additives (JECFA), and the Codex Committee on Food Additives and Contaminants (CCFAC) have proposed a limit of 0.1 mg kg^{-1} for Cd in cereals, pulses and legumes due to the risk associated with the long-term consumption of Cd-contaminated crops;[17,18] while the European Community has a limit of 0.2 mg kg^{-1} for wheat grain,[19] and the maximum tolerable limit of Cd for humans proposed by FAO/WHO is 70 µg a day.[11,16]

Through its effects on various biochemical and physiological processes in plants, Cd could inhibit plant growth and cause cell death above critical levels.[20,21] Cadmium-induced growth reduction might be explained on the basis of inhibition of carbon fixation due to a decrease in photosynthetic rate and chlorophyll content.[22] Cadmium in soils could induce water stress in plants by decreasing stomatal conductance, transpiration

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rate and leaf relative water contents.[23] This is the result of physiological damage from decreased intracellular space and amount of chloroplast, and cell enlargement.[24] Cadmium toxicity induces the production of reactive oxygen species (ROS) which may result in membrane damage, and the destruction of cellular organelles and biomolecules.[25] These damages can enhance the translocation of Cd to aerial parts. Moreover, the lack of energy for Cd sequestration in roots may also be responsible for its translocation from roots to aerial parts.

According to Verkleij *et al*.[26] there is a duality in plant tolerance to heavy metals. Certain heavy metals like iron (Fe), copper (Cu), zinc (Zn) and manganese (Mn) at low concentration are beneficial for plants either through improving plant growth, biofortification, or both, and in this way beneficial for all living organisms in the food chain. However, heavy metals also exert damaging effects on plants at similar or higher concentration depending on the specific/tolerance mechanisms the plants use to protect themselves, but could also produces compounds with some deleterious potential for organisms, including man. High levels of heavy metals in soils, including Cd, could damage biomemebranes and cause uncontrolled uptake or translocation of Cd in plants. In addition to this toxicity-induced Cd accumulation, plants may accumulate significant amounts of Cd in different parts without any significant toxicity and yield loss.[27] Hence, programs for safe food production from Cd-contaminated soils should concentrate on the minimization of Cd accumulation instead of the mitigation of Cd toxicity. Moreover, accumulation of Cd in edible plant parts is more important than total plant uptake.[28]

It is necessary to minimize the entry of Cd into the food chain because of the number of associated health risks. Many strategies have been devised to minimize Cd toxicity and to check its entry into the food chain. Selection and breeding of crop plants/cultivars that accumulate low Cd in the grain and other edible plant parts is one of these approaches.[29–32] It seems an attractive approach to change the Cd profile of crop plants and the benefit continues generation after generation in plants through the seed. Lower Cd durum wheat and sunflower cultivars have been introduced in the last few years; improving cultivars takes time and money, but provide the persistent benefit of lower dietary Cd. Differential Cd uptake and distribution may be the result of differences among cultivars in the capacity to retain absorbed Cd in the roots or to variations in xylem loading or Cd retranslocation in the phloem.[33,34] Structural and physiological characteristics of cultivars may lead to different capabilities of retaining Cd inside the roots and, in turn, to the observed variation in Cd partitioning.[33] However, there are constraints to using this approach to produce low-Cd food as it is very time consuming to develop and test a new cultivar. Generally, it takes 5–10 years to develop new cultivars.[35] Moreover, low Cd accumulation adds an additional trait to an already existing long list (yield, quality, disease resistance and many other characteristics) required of a new cultivar.[35] It also implies that it is very difficult to manage the low Cd accumulation trait with a number of other characteristics in the same cultivar.

Phytoextraction is another approach to minimize Cd entry into the food chain, which involves the use of hyper-accumulator plants to remove Cd from soil.[36,37] But the problem is that hyper-accumulator plants are slow growing and produce very low biomass and a long time is required, perhaps several years, to remediate the contaminated site.[38] Moreover, the disposal of Cd-accumulated plant material is also of great concern and methods for the disposal of metal-enriched biomass have not yet been well developed.[39] Similarly, crop rotation,[40] liming[41] and the use of other organic and inorganic amendments[40] are some other approaches being used to remediate Cd-contaminated soils, but these approaches are time consuming and require extra resources.

Use of plant nutrients to alleviate Cd toxicity in plants is a relatively inexpensive, time saving and effective approach to avoid Cd contamination of food. Additionally, for better plant growth an adequate and balanced supply of nutrients is essential in proper amounts and at the correct time. Growers are already applying nutrients to obtain good crop yield, so to alleviate Cd toxicity the proper management of these plant nutrients is needed, keeping in mind the interactions between Cd and plant nutrients. Several of the plant nutrients have many direct as well as indirect effects on Cd availability and toxicity. Direct effects include decreased Cd solubility in soil by favoring precipitation and adsorption,[41–44] competition between Cd and plant nutrients for the same membrane transporters,[45–47] and Cd sequestration in the vegetative parts to avoid its accumulation in grain/edible parts.[48–50] Indirect effects include dilution of Cd concentration by increasing plant biomass[51] and alleviation of physiological stress.[52–56] Relatively high doses of N and some other plant nutrients can cause soil acidification,[57] enhancing the solubility and bioavailability of heavy metals including Cd.[50] Moreover, fertilizers determine Cd speciation and complex formation, which could affect Cd movement to roots and its absorption into the roots. Fertilizer application also affects the rhizosphere composition, root growth and overall plant growth,[58] and that, in turn, modifies the availability, absorption and accumulation in different plant parts.

Plant nutrients affect the activity and bioavailability of Cd in the soil–plant environment. Therefore, it is of great importance to study the interaction of Cd with plant nutrients in soil–plant systems to use it as a tool to minimize the accumulation of Cd in edible plant parts.[27] The main objective of this review is to highlight the relationships of plant nutrients with Cd to understand how the management of plant nutrients is useful in reducing Cd availability in soil, root absorption, translocation to shoot and then grain, and how these nutrients are helpful in the development of tolerance against Cd toxicity and the reduction of Cd accumulation in plants, especially the edible parts.

FACTORS AFFECTING THE BIOAVAILABILITY OF CADMIUM

It is not necessary that all the Cd present in soil is available for plant uptake. The term bioavailability is defined as 'the part of the total concentration of a chemical that is available to receptor cells (plants, microorganisms, etc.)'. The part of soil Cd concentration available to plants is called bioavailable Cd. This bioavailable concentration is the main concern regarding its uptake and accumulation in plants rather than the total concentration of Cd in soil. So in any study, both the total concentration as well as the bioavailable concentratioin should be measured. A number of factors affect Cd bioavailability in soil, including soil pH, organic matter presence of other ions, root exudates, types and cultivars of crop plants, and plant age.[59,60] These factors influence the solubility of Cd compounds and the release of Cd into the soil solution or affect the ability of plants to take up Cd from soil.[61] Some have positive effects while others have negative effects on Cd bioavailability.

Among soil factors affecting Cd availability, soil pH is the most important.[62] There is an indirect linear relationship between soil pH and Cd bioavailability, i.e. with a decrease in soil pH, metal uptake by plants increases.[63,64] So, it may be possible that in

Cd-contaminated acidic soils availability is greater as compared to neutral and alkaline soils. Cadmium availability in such soils can be decreased by manipulating soil pH through the use of various amendments including liming[41] and application of base-rich fertilizers. Application of some fertilizers, such as NH_4^+ fertilizers including urea, ammonium sulfate and monoammonium phosphate (MAP), can enhance Cd availability by lowering pH.[10,50] Organic matter content is another important soil factor that affects Cd availability in soil as it is capable of retaining metal cations. Organic matter acts as a primary sorbent of heavy metals in organic forest soils.[65] Sauvé *et al*.[66] conducted a study in Canada on organic forest soils, and found that soil pH and total metal concentration were not consistent indicators of bioavailable Cd. The sorption affinity of soil for Cd was 30 times greater due to presence of organic matter as compared to mineral soil. So, in Cd-contaminated soils, use of various organic amendments such as farm yard manure (FYM), composts, bio-solids and bio-solid compost can effectively reduce Cd availability to plants.[40]

The presence of other ions also has a great influence on Cd availability. This influence may be due to ionic strength,[67] complexation[68] and competition for soil exchange sites or root surface exchange sites.[41] Ionic strength of the growth medium affects Cd availability inversely, which indicates that the lower the ionic strength of growth medium, the higher the metal concentration taken up by plants.[67] Cadmium is also found to form complexes in the presence of Cl^- which results in increasing solubility and thus availability of Cd.[68] Cations like Ca^{2+}, Mg^{2+}, Zn^{2+} and Mn^{2+} compete with Cd for uptake by plants[41,42,69] and for exchange sites in soils.[68]

Different plant species vary greatly in metal uptake from soil.[70] Some plants, including maize, pea, oat and wheat, are low accumulators of heavy metals, while some leafy vegetables, like spinach and lettuce, accumulate a high metal concentration in their leaves.[40] In general, Cd accumulation is greater in leaf vegetables, less in root vegetables and lowest in grain crops.[71] Wheat accumulates much higher Cd concentrations than other cereal species.[40] The behavior of heavy-metal accumulation also varies from cultivar to cultivar as there are large genotypic differences for metal accumulation in many species.[30–32] Jamali *et al*.[32] conducted a pot culture experiment on four newly bred wheat cultivars (Anmol, TJ-83, Abadgar and Mehran-89) to reduce the potential of heavy-metal accumulation from amended sludge. The results showed that in two wheat cultivars (TJ-83 and Mehran-89) heavy-metal concentration was more than in the other two cultivars (Anmol and Abadgar) grown under similar amended sludge treatments.

The release of root exudates is an important plant factor that affects Cd bioavailability. Root exudates are part of the photosynthates of plants (12–40%) that are released through roots into soil, consisting of sugars, polysaccharides, amino acids, peptides, proteins and some organic acids.[72] Organic acids released by plants can bind and sequester heavy metals in soil[73] and this mechanism protects roots from the toxic effects of heavy metals[74] and may also decrease Cd uptake by plants. As these exudates are photosynthates of plants, by improving plant nutrition, release of root exudates can be modified.

ESSENTIAL PLANT NUTRIENTS

Proper nutrition is a basic requirement of every living organism. There are now 17 elements which are considered essential for plants to complete their life cycle. These essential plant nutrients are divided into two categories: macronutrients and micronutrients. Macronutrients include carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulfur (S). Micronutrients are zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), boron (B), molybdenum (Mo), chlorine (Cl) and nickel (Ni).[75] Although silicon (Si) is not essential, it is considered a beneficial plant nutrient. These plants nutrients are not only required for better plant growth and development, but also helpful to alleviate different kinds of stresses like heavy-metal stress.[41,47,56] The role of some important macronutrients and micronutrients, along with Si, as antagonists to Cd accumulation in grain/edible parts to minimize its dietary intake is discussed here.

Nitrogen

Nitrogen (N) is an essential macronutrient deficient in most soils, especially in arid and semi-arid regions.[76] It is an important component of many structural, genetic and metabolic compounds in plants,[22,77] and of the total nutrients absorbed by plant roots, 80% is contributed by N.[78] It is taken up by plants both in the form of ammonium (NH_4^+) and nitrate (NO_3^-), and in plants NO_3^- is also reduced to NH_4^+ for assimilation into plant organic N.[56] For better crop growth, a combination of ammonium (NH_4^+) and nitrate (NO_3^-) sources is preferred.[79] Possible mechanisms to minimize Cd accumulation in cereals and legumes by improving N nutrition are presented in Fig. 1.

Rhizosphere chemistry, especially pH, is very important in determining the availability and absorption of nutrients and metals including Cd from soil.[80,81] Roots have a profound influence on soil pH and it has been found that, in general, pH of the rhizosphere is lower than bulk soil. Rhizosphere acidification occurs as a result of NH_4^+ nutrition due to the release of protons (H^+) by root cells or nitrification of NH_4^+, and this induced acidification can promote mobilization of a localized metal in neutral to alkaline soil contaminated with a particular heavy metal like Cd.[50,82] The type of N fertilizers applied will determine whether there would be a decrease or an increase in Cd uptake with its application. Compared to NO_3^- fertilizers, NH_4^+-containing fertilizers could result in enhanced Cd uptake due to a decrease in soil pH. However, the effect of counter ions in fertilizers like Ca in $Ca(NO_3)_2$ cannot be overlooked. If applied at high rates, Ca in fertilizers could replace Cd present on soil particles, resulting in higher Cd concentration in the soil solution. However, this additive effect of counter ions like Ca on increased solubility and uptake of Cd is only possible at higher pH. At lower pH, the major effect on increased Cd uptake from soil would be of NH_4^+ leading to a decrease in soil pH. In contrast to many researchers, Xie *et al*.[83] recently investigated the effect of N form (NO_3^- vs NH_4^+) on growth and uptake of Cd and Zn by *Thlaspi caerulesscens* in hydroponics and rhizobox experiments and found that plants fed NO_3^- accumulated much more Cd than plants supplied with NH_4^+, even though the rhizosphere pH was lower in plants treated with NH_4^+. This NO_3^--induced Cd accumulation was speculated with the increase in organic acid exudation due to the accumulation of NO_3^- at the root surface. These contrasting results could also be related to the plant species used in the various experiments.

Contrasting results have been reported regarding the influence of N fertilizer on the uptake of Cd from soils. Increased N application would result in more biomass production by increasing the photosynthetic rate. As a result, Cd concentration in wheat grain would decrease due to the dilution effect[51] as more biomass production sequesters more Cd in vegetative parts and very little

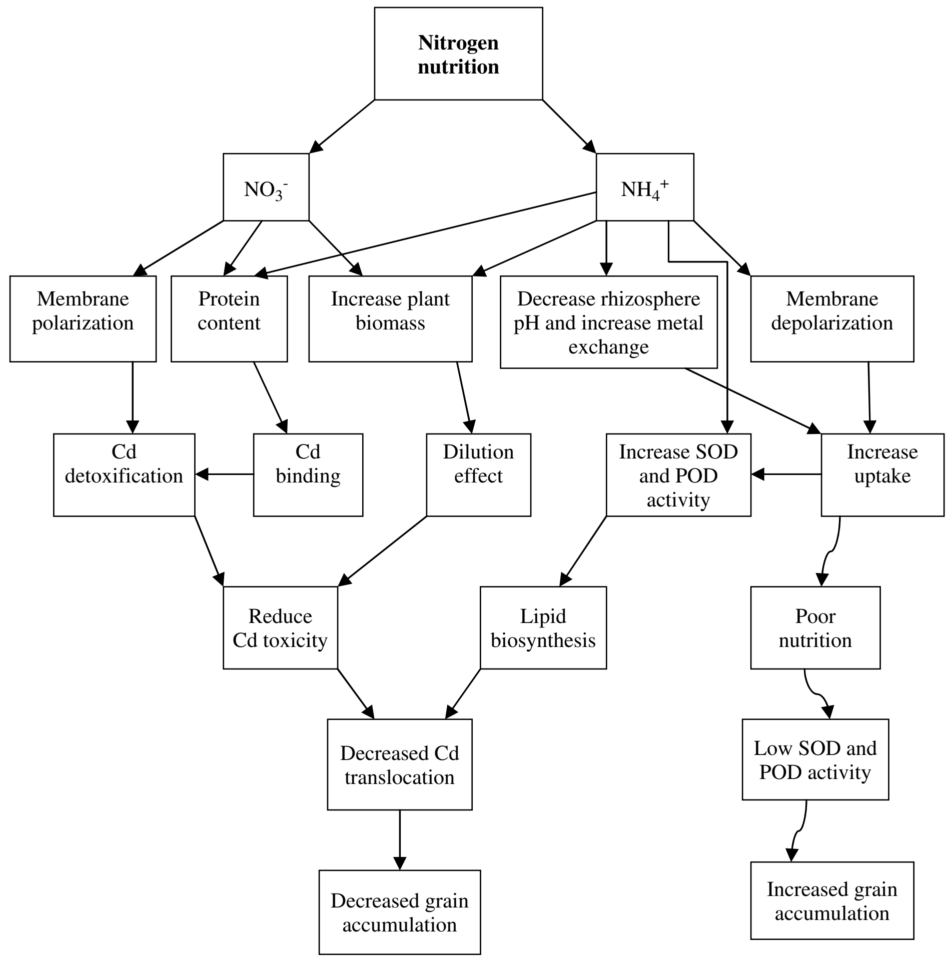

Figure 1. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving nitrogen nutrition (adapted from References 50–52,56,82).

moves into the grain.[51] But Wangstrand *et al.*[84] claimed that with application of a higher rate of N, aimed not to enhance biomass production but to increase protein content of bread wheat grain, more Cd might be accumulated in plants. Time of application might be important, i.e. if an extra dose of N is applied at the vegetative stage, it can enhance biomass production; however, during the grain filling stage, the application of an extra dose of N can increase grain Cd concentration as NH_4^+ fertilization increases the availability of metal ions due to soil acidification.[50] So, it is recommended that in Cd-contaminated soils more N application should be done at the vegetative stage to increase biomass production, while high N doses during the grain filling stage to increase protein content should be avoided. This strategy can reduce the Cd accumulation in grain.

One possible mechanism for alleviating Cd toxicity by the dilution effect might be the increase in soluble protein content[52] which causes sequestration of the mobile form of Cd to the immobile form by binding to some protein molecules. The dilution of Cd concentration in the plant may also prevent membrane damage which is due to the high concentration of Cd on membrane surfaces. Pankovic *et al.*[52] performed an experiment to analyze the effect of N nutrition on photosynthesis in Cd-treated sunflower plants. Three low levels of Cd (0.5, 2 and 5 mmol m^{-3}) in combination with three N treatments (2, 7.5 and 10 mol m^{-3}) were applied to young sunflower plants. They found that at 7.5 mol m^{-3} N, when soluble protein and Rubisco content were maximized, inhibition of photosynthetic activity by Cd was the lowest. From this study, it was concluded that N supply could be manipulated as a means of decreasing Cd toxicity to plants but optimum [N] to [Cd] ratios must be determined for specific plant species and growth conditions.[52]

Ammonium ions cause cell membrane potential depolarization, which results in the influx of NH_4^+ into the cytoplasm of the root cells.[50] This increased uptake of NH_4^+ reduces the Cd uptake by cells. But this mechanism increased the translocation of Cd from root to shoot in sunflower plants possibly due to lack of a detoxification mechanism.[50] However, activities of superoxide dismutase (SOD) and peroxidase (POD) increased in the case of NH_4^+ nutrition, which is considered a protective mechanism against stress. Peroxidase is also involved in lipids biosynthesis which acts as a physical barrier against heavy metals.[56] On the other hand, in plants fed with NO_3^- most of the Cd accumulated in roots due to the detoxification mechanism.[50] Jalloh *et al.*[56] conducted a pot experiment to study the effects of various N fertilizer forms on antioxidant capacity and grain yield of rice (*Oryza sativa* L.) under Cd stress. They observed a higher Cd concentration and less N accumulation in plants treated with NO_3^--N, and the opposite (results) in the case of NH_4^+-N treatment. Observation of plants indicated antagonistic interactions between NH_4^+-N and Cd, and synergetic interactions between NO_3^--N and Cd. An increase in

SOD and POD activities was also more significant in plants treated with NH_4^+-N, which is considered a protective mechanism against Cd stress. The authors argued that Cd stress could be alleviated by choosing a specific form of N fertilizer.

In light of the above findings, it can be concluded that crop species and the N source, rate and timing of application are important considerations in order to understand the role of N to minimize Cd accumulation in edible portions of crop plants. Still, further research is needed to fully understand how N nutrition plays its role to minimize Cd accumulation in plants, through mechanisms at the molecular level.

Phosphorus

The quantity of P in soils is less than N and K. Total P concentration in surface soils varies from 0.005 to 0.15%.[85] After N, it is the second most deficient plant nutrient and is applied to plants as fertilizers. More than 30 million metric tonnes of P_2O_5 in phosphate fertilizers per year are used worldwide, of which more than 99% is derived from rock phosphate.[86] The use of P fertilizers has increased crop production many fold, possibly through narrowing the N : P ratio. However, the use of phosphatic fertilizers can cause the contamination of soils with trace heavy metals like Cd, Cu, Mn, Ni, Pb and Zn which are naturally present in rock phosphate.[87,88] Possible mechanisms to minimize Cd accumulation in cereals and legumes by appropriate P nutrition are shown in Fig. 2.

Application of some P fertilizers like mono-ammonium phosphate (MAP) could increase solubility of Cd by lowering soil pH, resulting in enhanced accumulation of Cd from soils. In field experiments conducted in Manitoba, Canada, Grant and Bailey[10,89] studied the influence of P and Zn fertilizer management on Cd accumulation in flaxseed and durum wheat. They found that both concentration and accumulation of Cd in flaxseed and durum wheat increased by the application of P as MAP. In another study in Manitoba, application of MAP and potassium chloride (KCl) tended to increase Cd concentration in malting barley.[90] These increased concentrations of Cd in grain might be due to increased solubility of Cd in soils which accelerated the Cd uptake by plants. The effect of P fertilizer application on the solubility of Cd and Zn in soils was investigated by Lambert *et al.*[88] In both field and laboratory experiments, they found that application of P fertilizers containing Cd and Zn enhanced Cd in the soil extract, while Zn concentration in almost half of the treatments decreased as compared to the control. However, in neutral/alkaline soils, application of fertilizer MAP causes slight change in pH.[91] This minute change in pH will increase availability of a localized heavy metal (Cd) to a very small extent.

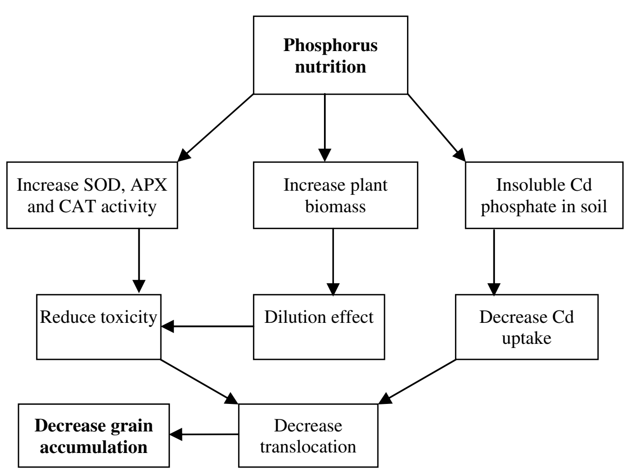

Figure 2. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving phosphorus nutrition (adapted from References 25,27,44,92–94,96,98).

Phosphate fertilizers on the other hand, also decrease the mobility of Cd in soil by changing mobile forms of Cd to an immobile form of Cd phosphate,[27,44] which is considered a key (extrinsic) mechanism of decreasing Cd availability to plants. Matusik *et al.*[44] compared the effect of different P compounds (K_2HPO_4, $NH_4H_2PO_4$ and 'Polifoska 15' fertilizer) over a pH range of 4.0–9.0 and for reaction times of 2–1440 h. A reduction of greater than 99% in available Cd concentration was observed for all forms of phosphate between pH 6.75 and 9.00. Bolan *et al.*[92,93] explained phosphate-induced immobilization of Cd in soils by: (1) phosphate-induced Cd^{2+} adsorption; and (2) precipitation of Cd as $Cd(OH)_2$ and $Cd_3(PO_4)_2$. Several mechanisms were advanced for the immobilization mentioned which include: (1) an increase in pH; (2) an increase in surface charge; (3) co-adsorption of phosphate and Cd as ion pair; and (4) the surface complex formation of Cd on the phosphate compound.

Phosphorus application may increase plant growth and yields which can neutralize the toxic effect of Cd by the dilution effect. Wang *et al.*[94] found that addition of external P reduced toxic effects of Cd on P-treated plants as compared to the control (no P applied). In a greenhouse study, Dheri *et al.*[27] reported that application of P fertilizer as KH_2PO_4 to spinach (*Spinacia oleracea* L.) decreased the concentration of Cd in spinach plants by reducing the diethylene triamine pentaacetic acid (DTPA)-extractable Cd in soil, while also enhancing dry matter yield of both shoot and root. They concluded that application of P was effective for *in situ* immobilization of Cd in mildly Cd-contaminated soil, and their findings suggested that Cd toxicity in spinach plants grown in mildly Cd-contaminated soils can be minimized by phosphate-P application. Phosphorus is involved in glutathione (GSH) biosynthesis[95] which is commonly suggested as a precursor in phytochelatin (PC) synthesis. These phytochelatins compartmentalize Cd into vacuoles by forming Cd/PC complexes.[48] Wang *et al.*[94] observed an increase in GSH content in P-treated plants as compared to the zero-P control.

Reactive oxygen species (ROS) are continuously produced as byproducts of different metabolic reactions particularly under stress, causing damage to biomolecules like membrane lipids[96] and proteins.[97] Certain antioxidant enzymes are produced by plants in response to oxidative stress to mitigate the effect of ROS such as SOD, ascorbate peroxidase (APX) and catalase (CAT).[96] Superoxide dismutase converts the superoxide radical into hydrogen peroxide (H_2O_2) and oxygen (O_2).[98] Hydrogen peroxide is still damaging and is further converted to H_2O by the action of CAT and APX.[96] Wang *et al.*[94] found that the activity of these antioxidants increased under Cd stress by the application of P, which mitigates the oxidative stress and prevents membrane damage. So P can partly alleviate Cd toxicity. The actual mechanism is still unclear and needs further research.

In summary, there is no well-documented evidence to identify the intrinsic mechanism for the development of plant tolerance against Cd by P nutrition. Extensive research is required to understand the role of P nutrition in developing plant tolerance against Cd.

Sulfur

Sulfur (S) is an essential macronutrient that plays a key role in protein synthesis. It is an important structural component of many

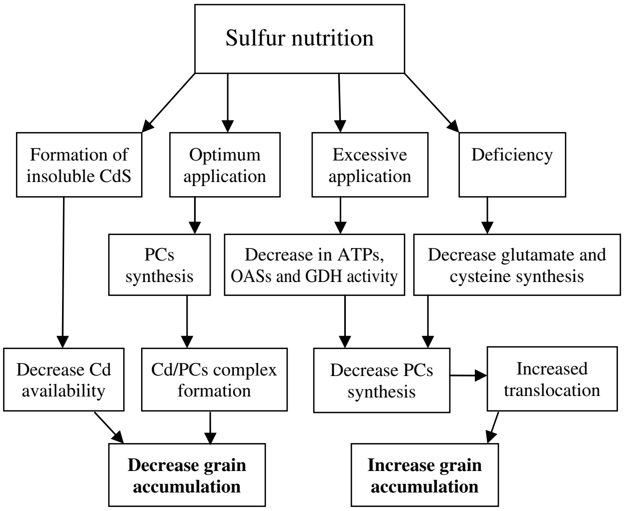

Figure 3. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving sulfur nutrition (adapted from References 48,49,72,104–106).

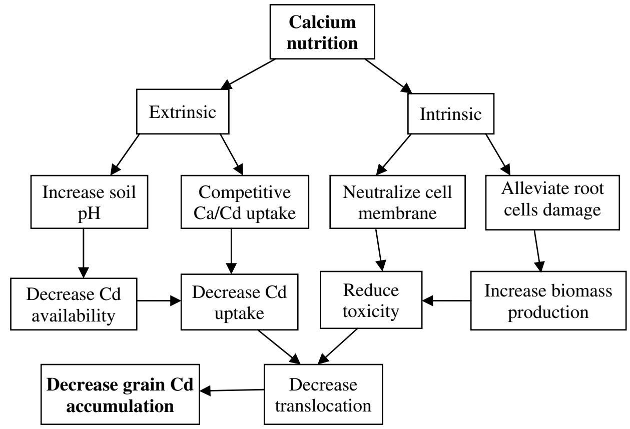

Figure 4. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving calcium nutrition (adapted from References 41,46,55,108).

co-enzymes and prosthetic groups such as feredoxins important in N assimilation. Thus, S plays an important role in plant growth and development. Sulfur deficiency has become a recently emerging problem, which results in decreased crop yield and quality.[99] In the past, application of N fertilizers like ammonium sulfate and ammonium superphosphate, and atmospheric S depositions were enough to meet the S requirements of crops. However, at present, atmospheric S emissions have been reduced to a great extent and the use of high analysis fertilizers like urea and triple superphosphate or di-ammonium phosphate have caused S deficiency in many soils.[100] Possible mechanisms to reduce Cd accumulation in cereals and legumes by proper S nutrition are presented in Fig. 3.

Sulfur causes the production of H_2S in soil, which results in the formation of insoluble CdS making Cd unavailable to plants. This is due to the fact that application of sulfate fertilizers causes vulcanization in the soil and produces H_2S.[72] Hassan *et al.*[22] investigated the effect of different N fertilizer forms on Cd uptake and its toxicity in rice plants, using two Cd levels (0 and 1 µmol) and three N forms $(NH_4)_2SO_4$, NH_4NO_3 and $Ca(NO_3)_2$. The minimum growth inhibition, and the highest photosynthetic rate and chlorophyll content were recorded in plants fed $(NH_4)_2SO_4$. Hassan *et al.*[22] speculated that S in nutrient solution reduces the availability of Cd by forming insoluble CdS. On the other hand, Mclaughlin *et al.*[9] observed that under irrigation using high sulfate water content, the Cd uptake by crop plants was high due to formation of sulfato complexes. Sulfur also enhances glutathione (GSH) synthesis which is considered an important defensive mechanism against metal stress.

Cadmium toxicity can induce deficiency of several macronutrients in plants.[101] So, it is possible to minimize some of the Cd-induced negative effects through the optimum use of mineral nutrients.[8] Sub-optimal S nutrition in Cd-exposed plants can induce S deficiency due to synthesis of PC.[102,103] Metals like Cd are detoxified by chelation of metal ions with high-affinity phytochelatins, which seems an important defensive response against metal toxicity.[49] But the availability of reduced S is an essential factor for PC synthesis.[104] Cobbett[105] proposed that PCs reduce activity of Cd in cytosol by forming Cd–PC complexes. These complexes are compartmentalized into vacuoles possibly by means of an ATP-binding transporter present in tonoplast.[48] But the availability of reduced S is essential for PC synthesis.[104] So, optimum S nutrition is helpful for reducing Cd translocation within the plant body.

Cadmium toxicity induces rapid synthesis of PC thiol-based complexing substances.[103] Phytochelatins are glutamate- and cysteine-rich proteins, so sulfate and nitrate assimilation pathways are important in PC synthesis: S metabolism enzymes are required for synthesis of cysteine, while enzymes of N metabolism are essential for synthesis of glutamate.[106] In S-deficient Cd-treated plants, ATP sulfutylase (ATPS), *O*-acetylserine (OAS) and glutamate dehydrogenase (GDH) are increased, maybe partly due to a defensive mechanism, which is based on PC synthesis.[106] Thus, optimum S nutrition should be recommended, which is not only important for better plant growth and development, but is also required for detoxification of Cd by PC synthesis, and to develop tolerance in plants against Cd toxicity.

Calcium

Calcium (Ca) is a macronutrient essential for plants as well as animals. It occupies much of the exchange sites in neutral and calcareous soils, while in acidic soils Ca^{2+} and Al^{3+} dominate the cation exchange capacity.[85] Plants absorb Ca^{2+} from the soil solution via mass flow and root interception. Possible mechanisms to check Cd accumulation in cereals and legumes by improving Ca nutrition are shown in Fig. 4.

In some studies, it has been shown that Ca as a plant nutrient can help to alleviate Cd toxicity. Both Ca and Cd compete for the same Ca channels in plants.[46] Cadmium toxicity in animals may be affected by interactions between Ca and Cd.[107] Choi *et al.*[108] showed that plant Cd tolerance in tobacco plants was increased by Ca application due to formation of Cd–Ca-containing crystals, and removal of these crystals through the head cells of trichomes. Suzuki[55] investigated the effect of Cd toxicity on root growth inhibition in *Arabidopsis* seedlings supplemented with Ca. Retardation of root growth was observed, increasing cell death at growing points (root tips). On the other hand, application of Ca alleviates root growth inhibition due to a decrease in cell death.

Several mechanisms have been proposed to explain the effect of Ca on the alleviation of Cd toxicity. This may be due to the fact that the plasma membrane surface is usually negatively charged, and a high concentration of Ca^{2+} would neutralize the membrane surface and minimize the toxic effect of Cd. It may also be due to the high concentration of Ca^{2+} around Ca channels which may decrease the influx of Cd.

Tlustos *et al.*[41] determined the effect of liming with CaO and $CaCO_3$ on metal ion uptake by spring wheat in both pot and rhizobox experiments. They observed a 50% decrease in uptake for Cd, 80% for Zn and 20% for Pb. This can be explained on the basis of increased soil pH, which immobilizes metals in the soil. Another possible reason might be the high availability of Ca^{2+}, which decreases the uptake of other metals. So, Ca can be helpful to alleviate Cd toxicity (at least partly) in the soil–plant environment.

Zinc

Zinc (Zn) is an important micronutrient essential for plant growth and development. Zinc status in soils and plants has a vital role in plant Cd accumulation. Previous research to understand Cd and Zn interactions has shown inconsistent results. Wu and Zhang[109] proposed that the application of Zn can alleviate the physiological damage caused by Cd toxicity. In an hydroponic experiment, Hassan *et al.*[54] reported that application of Zn alleviated Cd toxicity by improving photosynthesis. Hart *et al.*[42] suggested that Zn supplementation reduced Cd tissue concentration probably by inhibiting Cd uptake into roots. Possible mechanisms to prevent Cd accumulation in cereals and legumes by appropriate Zn nutrition are presented in Fig. 5.

Cadmium toxicity induces rapid synthesis of PC thiol-based complexing substances.[103] Phytochelatins form Cd–PC complexes and Cd is sequestrated in the vacuole of root cells, resulting in decreased Cd translocation from roots to shoots.[54] But in the presence of Zn, Zn–PC complexes are formed,[110] which can increase the concentration of free Cd and, as a result, Cd translocation from root to shoot is enhanced. Zhu *et al.*[111] showed that Zn alleviated Cd toxicity in plants only at toxic Zn levels and did not improve plant growth, because in this case Zn toxicity suppressed plant growth. Another study showed that Cd–Zn interactions are synergistic to each other and increasing the concentrations of Cd and Zn in soils could enhance the accumulation of these metals in crops.[112] Adiloglu[113] showed that Cd accumulation in plants is reduced with the application of Zn, and Cd accumulation is greater in Zn-deficient soils. Qiu *et al.*[47] proposed that increasing levels of Zn compete with Cd for the same membrane binding sites and transport systems and also limits Cd transport from phloem to grain. They showed that Zn had similar effects on Cd accumulation in winter wheat both in the long term (1 month) and the short term (24 h).

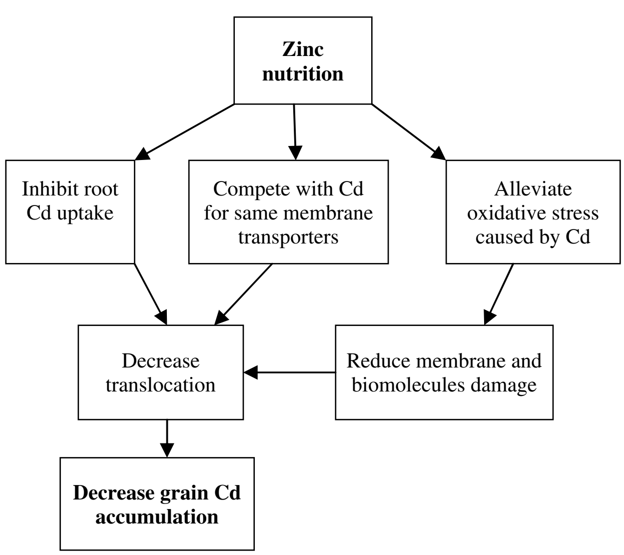

Figure 5. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving zinc nutrition (adapted from References 42,47,118,121).

Chemical similarity between Zn and Cd is thought to be the main cause of Cd toxicity in higher plants due to their interactions with each other. Xue and Harrison[114] identified a synergistic effect of Zn in relation to Cd uptake. They found that increasing the amount of Zn (>600 mg kg^{-1}) in soils containing high levels of Cd (10 mg kg^{-1}) resulted in a higher concentration of Cd in lettuce leaves. Similarly, Smilde *et al.*[115] and Kachenko and Singh[116] found high concentrations of Cd in leafy vegetables when soil Zn concentrations were increased. However, McKenna *et al.*[117] identified a strong antagonistic effect of Zn on the accumulation of Cd in leafy vegetables at low Cd concentrations. Moreover, Chaney and Oliver[87] suggested that a Cd : Zn ratio of <1.5% in food effectively provides protection against Cd-induced health impacts.

Cadmium causes oxidation of NADPH, resulting in production of superoxide (O_2^-),[118] because Cd and other transition metals act as catalysts to induce rapid free radical synthesis (ROS).[119] Cakmak and Marschner[120] observed that production of O_2^- increases under Zn deficiency. So, it is possible that O_2^- synthesis can be minimized by improving Zn nutrition. Aravind *et al.*,[121] using *Ceratophyllum demersum* L. (a free-floating hydrophyte), investigated the protective effects of Zn against ROS induced by Cd. Different levels of Zn (10, 50, 100 and 200 µmol Zn L^{-1}) against 10 µmol Cd L^{-1} were used. These authors observed that 10 µmol Cd L^{-1} triggered the production of H_2O_2 and O_2^-, while addition of Zn (10–200 µmol Zn L^{-1}) to Cd (10 µmol Cd L^{-1}) significantly reduced the production of these reactive oxygen species (ROS). Aravind *et al.*[121] argued that Cd enhanced the oxidation of nicotine adenine dinucleotide phosphate (NADPH), resulting in O_2^- synthesis and the application of Zn inhibited NADPH oxidation and reduced O_2^- production. It is inferred that, by improving Zn nutrition, oxidative stress caused by Cd can be alleviated to a great extent.

Iron

Iron (Fe) is an essential micronutrient for both plants and animals. In neutral-to-alkaline soils, it is present as insoluble Fe^{3+} compounds.[122] However, under anaerobic conditions in soils, the ferrous (Fe^{2+}) form is stable and readily available to plants. Plants reduce Fe^{3+} chelates to Fe^{2+} and transport via low-affinity iron transport systems through the plasma membrane, when Fe is not limiting.[123,124] Two distinct strategies are adopted by plants under Fe deficient conditions to assimilate Fe: (1) release of phyto-sidrophores (PS) by graminaceous monocotyledonous plants, which solubilize and take up Fe^{3+} by specific membrane receptors, and this Fe^{3+} is then reduced to Fe^{2+} in the cytoplasm (strategy II); and (2) acidification of the rhizosphere to enhance Fe availability, reduction of Fe^{3+} to Fe^{2+} by ferric reductase at the cell membrane and then transport to the cytoplasm (strategy I) in dicotyledonous and non-graminaceous monotyledonous plants.[123,124] Possible mechanisms to avoid Cd accumulation in cereals and legumes by proper Fe nutrition are presented in Fig. 6.

Ferrous ion (Fe^{2+}) may compete with Cd for the same membrane transporters, so an efficient supply of Fe^{2+} to plants may decrease

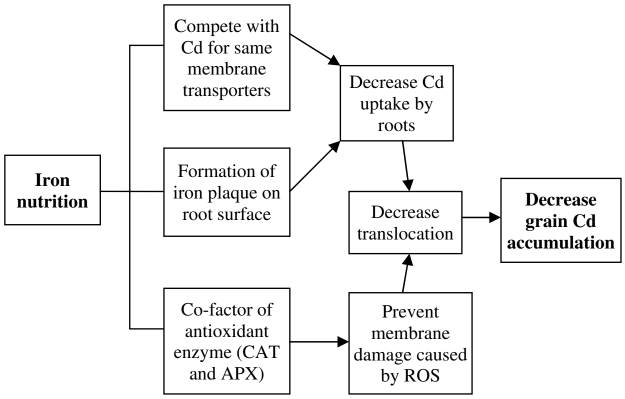

Figure 6. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving iron nutrition (adapted from References 125,126,129–131).

Cd uptake. But application of Fe^{2+} as $FeSO_4$ may oxidize to Fe^{3+} and become immobilized in soil. For this reason, Fe^{2+} should be applied to provide effective iron nutrition to plants. Sheng *et al.*[122] showed that soil application of Fe fertilizer (EDTA–Na_2Fe) significantly reduced Cd concentration in rice grain, shoots and roots, while soil application of $FeSO_4$ and foliar application of both $FeSO_4$ and EDTA–Na_2Fe markedly enhanced the Cd concentrations in shoots and roots. From these results, it can be concluded that the type of Fe fertilizer and the method of application might have marked effects on Cd accumulation in plants. Shao *et al.*[125] showed that Cd-induced oxidative stress in rice is alleviated by Fe nutrition.

Iron (Fe) is an integral cofactor of antioxidant enzymes such as catalase (CAT) and ascorbate peroxidase (APX).[126] So, by improving Fe nutrition, the activity of these enzymes may increase and this may prove an important defensive mechanism against ROS generated in the case of heavy metal stress.[96] However, free Fe is toxic to plants as it induces severe oxidative stress.[127] Sharma *et al.*[126] carried out a hydroponic experiment to investigate interference between Fe nutrition and Cd toxicity in barley seedlings. They observed increased CAT and APX activity under 25 μmol L^{-1} Cd at all Fe levels except 250 μmol L^{-1} where Fe induced CAT activity did not further increase due to Cd. The increased activity of antioxidant enzymes (CAT and APX) may alleviate the toxic effects of Cd by preventing membrane damage caused by ROSb.[25]

Iron deficiency can induce accelerated Cd accumulation in plants by regulating soil pH and redox potential (E_h), and this can be used as an important tool for phytoremediation of Cd from soil.[128] Formation of iron plaque on the surface of the root due to the release of O_2 and oxidants in the rhizosphere and the oxidation of Fe^{2+} to Fe^{3+} with the precipitation of iron oxide or hydroxide on the root surface is a common feature of aquatic plants such as rice.[129,130] Liu *et al.*[131] proposed that Fe plaque may adsorb and sequester Cd onto the root surfaces, and plant Fe nutrition can prevent Cd uptake by rice plants. Application of Fe to Cd-contaminated soils can increase Fe concentration and decrease Cd concentration in rice, leading to production of rice with high Fe but low Cd content, which is safe for humans.[131] Shao *et al.*[125] proposed that the inhibitory effect of high Fe nutrition on the expression of high affinity iron transport tends to reduce the uptake and accumulation of Cd in rice. They further hypothesized that both Fe and Cd compete for the common membrane bounded iron transport (carrier), so Cd toxicity in plants can be controlled by modifying Fe nutrition.

Manganese

Manganese (Mn) is a heavy metal as well as an essential micronutrient. It is also found to interact with Cd in soil–plant systems.[132] Possible mechanisms to minimize Cd accumulation in cereals and legumes by adequate Mn nutrition are presented in Fig. 7. Availability of Mn to plants is partly decreased by Cd addition to soil. Ramachandran and D'Souza[69] showed an antagonistic interaction between Cd and Mn, while Chen *et al.*[1] indicated a synergetic interaction of Mn with Cd. Baszynski *et al.*[45] suggested that Cd accumulation in plant tissues can be decreased by increasing the level of Mn possibly due to competition for the same membrane transporters.

Addition of Mn increases biomass production by improving root growth and enhancing NO_3^- uptake,[133] which reduces Cd toxicity. Alleviation of Cd toxicity prevents Cd translocation and accumulation in grain.[25] Cadmium replaces the central Mg^{2+} ion in the chlorophyll structure.[134] A high Mn level could alleviate Cd toxicity, especially by improving photosynthesis[53] because the application of Mn can partly restore the chloroplast structure damaged by Cd toxicity.[45]

Silicon

Silicon (Si) is the second most abundant element in soil after oxygen.[135] It occurs in two major forms: silica and oxides of silicon, and both types exist in crystalline and/or amorphous forms such as quartz, flint, sandstone, opal and diatomaceous earth silicates.[136] In soil solution it occurs as silicic acid at concentrations ranging from 0.1 to 0.6 mmol L^{-1}, which is two orders of magnitude higher than macronutrient P.[137] Plants absorb most Si in mono-silicic acid form from the solution in the transpiration stream. Despite Si being a ubiquitous and prominent constitute of plants, it is still not widely recognized as an essential nutrient for plants. However, it has been proved to be beneficial for better plant growth and development, especially in plants of the *Gramineae* family.[43,138]

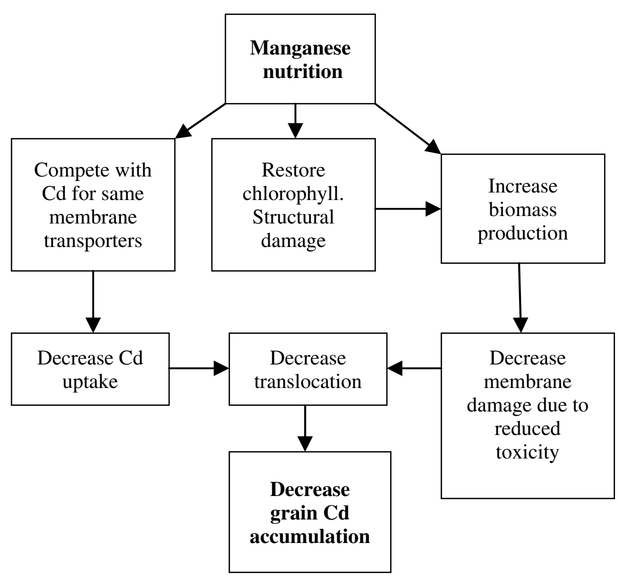

Figure 7. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving manganese nutrition (adapted from References 25,45,53,133,134).

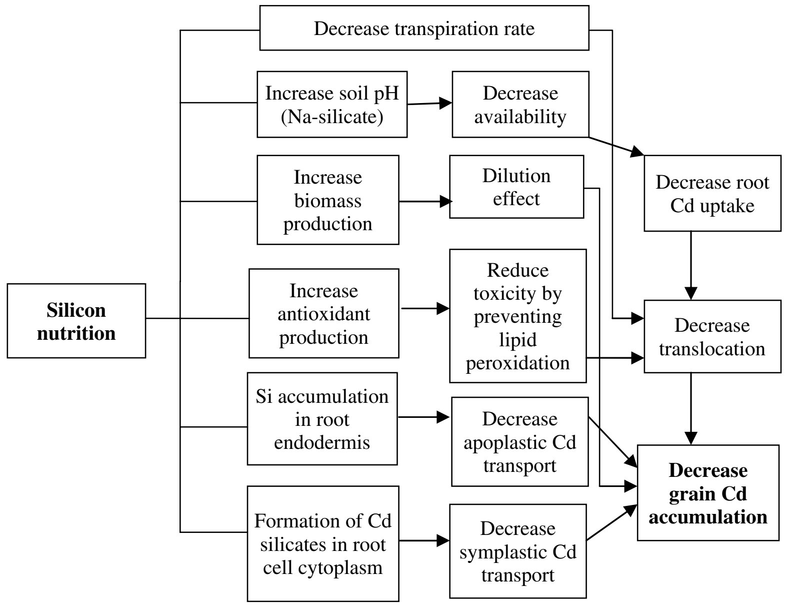

Figure 8. Possible mechanisms of minimizing Cd accumulation in cereals and legumes by improving silicon nutrition (adapted from References 135,140,143,147–149).

Possible mechanisms to reduce Cd accumulation in cereals and legumes by Si nutrition are presented in Fig. 8. Silicon can improve plant growth and tolerance to biotic and abiotic stresses.[137,139,140] In the case of heavy-metal stress, the presence of Si in the growth medium is helpful for reducing uptake and accumulation of heavy metals (like Cd) in rice,[43] wheat[141,142] and maize[143] seedlings.

Due to its high mobility in soil and plant system, Cd is readily taken up by plants. Among plant parts, roots are the major accumulator of Cd from their bathing medium.[144] The role of Si application in reducing Cd accumulation in edible plant parts has been well documented.[143,145,146] Increasing evidence is available showing that Si significantly interferes with root uptake and translocation of Cd from roots to shoots in plants. Based on a review of current literature, mechanisms responsible for low Cd accumulation in edible parts of plants are: (1) lower mobility of Si towards roots due to silicate induced pH rise in soils; (2) Si induced co-precipitation of Cd and Si in soil; (3) co-precipitation of Si and Cd at root surfaces; (4) decreased transport of Cd from roots to xylem; (5) reduced translocation of Cd from roots to shoots due to decreased evapotranspiration associated with Si deposition in cell walls, and as a double layer of polymerized Si in the cuticle; and (6) increased uptake of Ca with the application of Si, which decreased Cd uptake due to competition for uptake. The relationship between Si application and reduced Cd uptake has been extensively studied. As stated by Liang *et al.*[139] the mechanisms for Si-induced lower Cd in plants could be broadly classified as external factors (in soil) and internal factors (within the plant). In soils, application of Si as a chemical amendment resulted in significantly low phytoavailable Cd via increasing soil pH.[143] But this is not sufficient to explain the role of Si in the alleviation of Cd stress. Hodge[147] suggested that Si can change the plasticity of roots which is an important phenomenon in alleviating environmental stress. He proposed that the Si supply increased biomass production, which diluted the Cd concentration in shoots and roots. Moreover, application of Si increases Cd retention in roots and reduces Cd translocation to shoots by improving root growth.[148]

Cell wall bound Si in Si-accumulating plants inhibits Cd uptake significantly via the apoplastic pathway by covalently bonding with and capturing Cd as it diffuses through the cell wall and extra cellular spaces.[149] Silicon is capable of forming unstable silicates with heavy metals in the cytoplasm. This phenomenon inhibits symplastic transport of heavy metals.[140] In a review, Kirkham[63] concluded that few studies report Cd concentration in roots because of the difficulty in excavating them. Moreover, the author also concluded that it is also difficult to separate soil factors (e.g. an organic soil adhering to a root) that control Cd availability from root factors (e.g. root exudates). More studies were suggested by the author to distinguish Cd adsorption versus Cd absorption at the root, and what factors favor absorption over adsorption.

Foliar application of Si to reduce Cd accumulation in grain is a more effective and economical strategy, as compared to application of Si to the root. Liu *et al.*[135] studied the effect of foliar application of two silica sources on the alleviation of Cd stress and found that grain Cd accumulation in rice was significantly reduced by the application of Si, but had no significant effect on shoot Cd accumulation. The Cd–Si co-precipitation in cell walls restricts Cd translocation from shoot to grain, which alleviates the Cd toxicity and grain contamination.[135] The highest application efficiency of Si is obtained if it is applied at tillering to booting stage.[150] This may be due to the fact that plants absorb Si most effectively at this stage. Silicon nutrition can alleviate Cd toxicity to a great extent by improving plant tolerance to Cd stress. Concentration/rate of Si applied, placement method and timing of application (growth stage of the crop) are important considerations in this regard.

CONCLUSIONS

Cadmium is a toxic heavy metal for both plants and animals. In plants, Cd toxicity can cause decreases in photosynthetic rate, chlorophyll content, stomatal conductance, transpiration rate and relative leaf water content, and destruction of some physiological processes, which ultimately reduces plant growth and development. The consumption of toxic plant parts by animals and human beings can cause both acute and chronic disorders. Due to these risks, it is necessary to regulate Cd concentration in plants (primary producers) below permissible limits. The management of plant nutrients is very helpful to develop plant tolerance to Cd toxicity. Better plant nutrition can effectively alleviate Cd toxicity by a number of mechanisms. Application of some fertilizers, like phosphate fertilizers especially free from Cd, can decrease the availability of Cd either by fixation of Cd, or by forming insoluble or sparingly soluble phosphates of Cd. Appropriate application of plant nutrients increases plant biomass and grain yield, and decreases Cd concentration in grain and other edible plant parts by the dilution effect. Some plant nutrients, such as Ca, Fe and Zn, compete with Cd for the same membrane transporters. Plant nutrients also help to sequester Cd in vegetative parts by production of PCs and avoid Cd accumulation in grain. They help to alleviate physiological stress due to an excess of Cd. Thus, proper plant nutrition can be a good strategy to limit Cd in the food chain. The literature available, however, is insufficient to fully understand the role of plant nutrients to minimize Cd accumulation in grain or edible parts. Therefore, more research is required for a better understanding of the interactions between Cd and plant nutrients in soil–plant systems.

ACKNOWLEDGEMENTS

The authors thank Dr H.R. Kutcher for making valuable revisions to the manuscript.

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